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GAS-TIGHT, ALKALINE, BUTTON CELL-TYPE ACCUMULATOR

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GAS-TIGHT, ALKALINE, BUTTON CELL-TYPE ACCUMULATOR
[Gasdicht verschlossener alkalischer akkumulator in form einer knopfzelle]

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The invention concerns a gas-tight, sealed, alkaline accumulator in the form of a button cell with positive and negative electrodes that are arranged in the cell housing and that are separated by a separator.

The housing of a button cell is formed by a bowl-shaped base part and a cover made of nickel-plated steel sheet. The base part first receives the positive electrode, then an alkaline-resistant plastic material as separator follows; and on top of these parts there is the negative electrode. The electrodes and the separator are soaked with electrolyte. Between the negative electrode and the cover there is a spring that produces a tight contact between the electrodes and the cell housing. The cell bowl and the cover are insulated from each other by a plastic ring. By forming a bead and pressing the bowl edge tight, a perfectly closed seal is achieved.

Apart from their special construction, which distinguishes them from round cells, button cells are always designed for small capacities of up to approximately 1 Ah. In addition, while round cells are usually equipped with thin-layer, flexible wound electrodes, typical button-cell electrodes are compound electrodes made from a dry mixture, pressed into tablets, and installed so tightly in the cell that they are under a constant surface pressure.

The dry mixture is a combination of powder-like active material ($Ni(OH)_2$ in the case of the positive electrode), conductive material such as Ni-powder, and also trace amounts of a binding agent. For setting a discharge reserve in the cell, other additives of metallic cobalt or cobalt oxide are typical. The compound mixture is formed into a tablet during production by means of rotary presses.

However, the finished tablets also require, in addition to the conductive material already in the compound, outer armoring that is likewise conductive formed by a small basket made of nickel-wire web. After the parts are laid in this basket, the small basket must be sealed with a small plate made of the same wire web by striking an edge extending over the tablet over the cover plate. Thus, the repeated use of a press ram is required. Such processing steps limit fast production processes.

In addition, the conductive material additives can make up to 30 wt% of the compound mixture due to the poorly conductive, active $Ni(OH)_2$, e.g., Ni powder, and thus represent a considerable ballast of inert material. However, this material insert is indispensable for the necessary formation of a three-dimensional diverter structure by pressing the electrode. The volume capacity of the electrode is thus clearly limited. Typically, electrodes of at most 450 mAh/cm^3 are achieved.

Another disadvantage of the class related to this method is that for the electrode production, only mixtures can be used that can be processed in a round press. This assumes a granular compound that simultaneously exerts a certain lubricating effect on the stamping tool and enables volumetric metering. Not every particle distribution and not every binding agent is suitable for this purpose. Thus, there is minimal flexibility of the process with reference to receptor changes, particle size changes, and variations of the plastic binding agent additive.

The task of the invention is to provide a button cell that is based on the alkaline NiCd system or the NiH system with preferably hydrogen-storing alloys as negative electrodes and that is as free from the described disadvantages as possible.

The task is solved by means of a button cell, as defined in Claim 1.

The use of positive, pasted electrodes with a highly porous support frame made of metal foam (foam electrode) or from a metal felt or metal web (felt electrode) has proven to be very advantageous. The base metal is preferably nickel.

There are different techniques for generating a foam metal. The original material is usually a foamed plastic, e.g., polyurethane, with a sponge-like, open-pore structure. This is plated with the corresponding metal and the metal is annealed under an inert gas in order to remove the plastic. In this way, the plastic thermally decomposes and passes through pores in the nickel surface in the gas phase. According to another process, the "plastic sponge" is filled with metal powder and the entire piece is sintered. In a third method, metal powder is mixed with a pore-forming agent, the mixture is sintered or melted, and the remaining pore-forming agent is removed through etching.

A metal-fiber netting forms the base of the metal felt, usually attached like a web through sintering. However, it can also be obtained by means of plastic mat that is metallized and then heated under an inert gas. According to another known method, Ni from the gas phase is deposited on a plastic mat. Such mats have pore sizes between 100 and 1000 µm.

For producing positive electrodes according to the invention for button cells, e.g., a nickel foam with a porosity of 85-97%, preferably 95%, and with pore sizes between 50 µm and 500 µm, which is available as tape or sheet material, is precompressed to a defined thickness, e.g., 4 mm, and in a continuous or discontinuous process, a homogeneous, aqueous paste made of $Ni(OH)_2$ powder with different additives is introduced into this three-dimensional matrix.

The precompression sets an exact basis weight across the electrode thickness within a tolerance range of ±0.01 mm.

The additives include both binding agents in solid, liquid, or dispersed form, and also Co powder, CoO or $Co(OH)_2$ powder, as well as in one or the other case, connections with Zn or Cd. However, others are conductive materials usually found in button-cell electrodes.

The paste excess remaining on the substrate surface is then stripped and the electrode tape is dried at an increased temperature up to approximately 150°C in a continuous draw-through oven or also in parts.

Compression of the dried tape follows by means of rollers or a static press in order to guarantee inner contact of the individual powder particles. The electrode thickness is thus reduced from 4 mm to 2 mm. Such electrodes can be installed in button cells, e.g., with a diameter of 25.1 mm and a height of 6.7 mm (product series 170 DK).

In a final packaging step, circular, rectangular, or also hexagonal, individual electrodes are stamped from the tape, wherein the stamping tool is designed so that the stamping loss is as small as possible.

The advantages of the electrode equipment according to the invention for alkaline button cells have the result that in contrast to compound electrodes, the foam matrix requires absolutely no additives of conductive material, such as Ni powder. Their function is assumed by the three-dimensional sponge structure of the support, which only requires approximately 5% of the entire electrode volume. For compound electrodes (pressed powder tablets), the volume percentage of the conductive material is between 3 and 15%, and its weight percentage can be up to 30%. In an especially favorable case, the nickel basket, which surrounds the positive electrode as a diverter, can also be eliminated.

As a consequence from the especially light, favorable sponge structure of the foam metal support, the button cell electrodes produce exceptionally favorable specific volume capacities of 500-700 mAh/cm^3, wherein optimally up to 800 mAh/cm^3 can be achieved. The same applies for metal felt electrodes (felt electrodes). In contrast, the capacities for conventional button cell electrodes are only approximately 450 mAh/cm^3.

In an especially advantageous configuration of the button cell according to the invention, the capacity of the positive single electrode, which can be up to 90% higher, can be balanced by a negative electrode also of foam type. With this electrode combination, an increase of the cell capacity of approximately 40% can be achieved. However, this is only meaningful for the negative electrode of a NiCd button cell. For the intrinsic, conductive, negative alloy electrodes of NiH cells, an additional conductive frame is unnecessary.

The foam diverter frame is also mechanically more stable than the three-dimensional diverter structure in a compound electrode, which owes its cohesive strength to the corresponding production pressure, which, however, decreases noticeably over time due to volume changes in the nickel hydroxide during the cyclic charge/discharge operation. The decoupling of partial regions of the active compound, which occurs for positive compound electrodes at high cycle counts as a result of contact loss between particles of the diverter

structure, is not possible for the foam electrodes used in the button cells according to the invention.

Consequently, the foam electrode exhibits an essentially higher cycle stability in comparison with the compound electrode, so that for 1-hour charging and discharging, over 1000 cycles can be achieved.

Two figures are used to clarify the invention.

Figure 1 shows a button cell accumulator according to the invention in section.

Figure 2 shows a comparison of the capacity and lifetime behavior of a conventional button cell accumulator and one according to the invention.

According to Figure 1, the housing of the button cell 1 is formed by the bowl-shaped base part 2 and the cover 3 made of nickel-plated steel sheet. The bowl-shaped base part contains the positive $Ni(OH)_2$ electrode 4 with diverter structure according to the invention made of an open-pore nickel foam 5, while the cover part holds the negative electrode 6 according to the base electrochemical system, e.g., made of $Cd(OH)_2$ or preferably a hydrogen-storing alloy.

The electrodes are electrically isolated from each other by the intermediate plastic separator 7 and the housing is hermetically sealed by forming a bead on the bowl edge against the cover edge. A plastic ring 8 is used simultaneously as a sealing ring and as insulation of the bowl from the cover.

In Figure 2, the capacities C in mAh over the cycle count n are recorded for a button cell according to the invention with positive foam electrode (curve 1) and a conventional button cell (curve 2), wherein the curves each represent average values for a group of several test cells. In all cases, NiH cells are used. Each charge was done for a charging period of 4 h with 100 mA. Each discharge was done also with 100 mA to the final discharge voltage of 0.8 V.

This shows that the cells with positive foam electrodes are clearly superior to the cells with conventional positive compound electrodes both in terms of capacity and also relative to lifetime behavior.

Finally, in comparison with the compound or pressed powder electrode, the pasted foam electrode produces advantages relative to this method, because the ability to be processed on a round press does not have to be considered relative to the receptor for the active material. Thus, the morphology and particle size distribution of the used $Ni(OH)_2$, and also the other powdery additives, can be selected freely. The plastic binding agents can be selected completely freely between liquid, powdery, and dispersed types; the concentration of these binding agents can also be selected within wide limits.

On the other hand, the capacity, the load rating, and the cycle resistance of the button cells can be clearly improved through this flexibility relative to the used materials.

Claims

1. Gas-tight sealed alkaline NiCd or NiH accumulator in the form of a button cell having arranged in the cell housing positive and negative electrodes which are separated by a separator, in which the positive electrode has a support/diverter framework which is of a porous metal foam or metal felt, and in which the active material embedded in the support/diverter framework is free of additions of conductive agent.

2. Accumulator according to Claim 1, in which the metal forming the basis for foam or felt is nickel.

3. Accumulator according to Claim 1 or 2, in which the foam structure exhibits 85 to 97%, preferably approximately 95%, open pore volume.

4. Accumulator according to Claim 1 or 3, in which an approximately 5% proportion of the electrode volume is metal foam.

5. Accumulator according to one of Claims 1 to 4, in which the specific volume capacity of the positive electrode is from 650 to 700 mAh.

Fig. 1

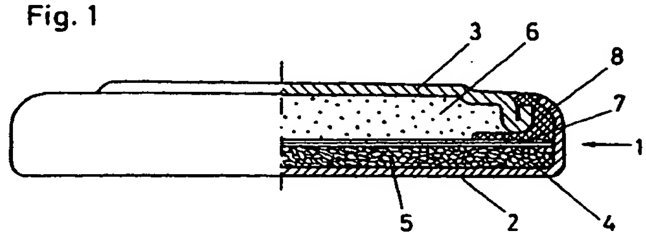

Fig. 2